Polymers with Pendant Alkyl Chains

THIS IS A UNITED STATES PATENT APPLICATION

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This application is related to, and claims priority from, United States Provisional Patent Application 60/411,907 filed Sept. 19, 2002 and hereby incorporates that application by reference.

BACKGROUND

Field of the Invention

The present invention relates generally to the field of polymers and more particularly to a class of polymers with pendant alkyl chains.

Description of The Problem Solved by the Invention

Polymers are very useful compounds that have a wide range of applications. It is known that different monomers allow the customization of properties of the polymer to suit the intended end use. A particular property that is very useful is that of hydrophobicity. A polymer with hydrophobic properties repels water and thus finds great use whenever this property is desired.

This type of polymer is particularly useful as a coating, especially if it can be sprayed on.

The most common method of adding hydrophobicity to a surface is the use of waxes. Stains and other coatings often incorporate a wax to increase the surface tension of water. The disadvantages are the possible adverse effect on the adhesion, short service life due to oxidation and the relative ease of removal, either by mechanical means or through washing and leaching if incorporated into a coating. This method would not be suitable for a low-drag marine coating. Another method is the use of PTFE polymer or incorporation of PTFE polymers into the coating. The use of PTFE is prohibitive in most coatings applications.

U.S. Patent 3,936,409 describes the synthesis of urea urethanes that can be used to protect various substrates from water, but these polymers do not have substantial hydrophobicity for many applications. U.S. Patent 3,936,409 is hereby incorporated by reference.

What is badly needed is a polymer that can be made cheaply and can possibly be sprayed on to form a water repellant coating.

SUMMARY OF THE INVENTION

The present invention relates to a hydrophobic polymer made by incorporating alkyl chains pendant to the main backbone of the

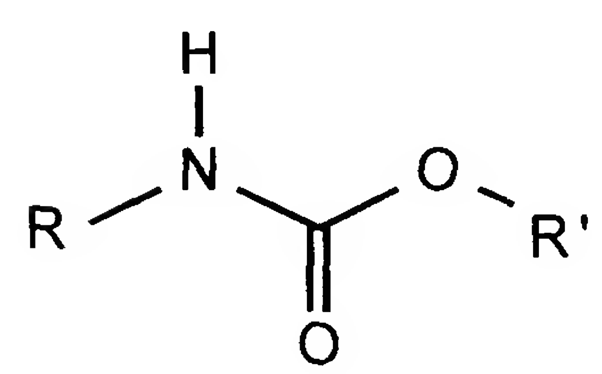
polymer. Alkyl chains of from about 6 to over 22 carbons are present in fatty compounds well known in the art. The present invention allows creating polymers with these alkyl chains pendant to the polymer chain. It is well known that synthetic and naturally derived starting materials such as tallow diamine or ethoxylated tallow amine typically contain a mixture of chain lengths with varying degrees of branching and unsaturation. The unsaturated positions in the final polymer can be made to cross-link in the presence of a catalyst to increase the hardness and reduce the effect of heat and solvent borne exposures.

The present invention can be a replacement to current monomers or additive to common polymers to replace or modify the current polymers to alter the properties of a polymer. The present invention adds the known benefits of fatty compounds to common polymers such as hydrophobicity, or in altering the HLB (hydrophilic lipophilic balance) of polymeric surfactants.

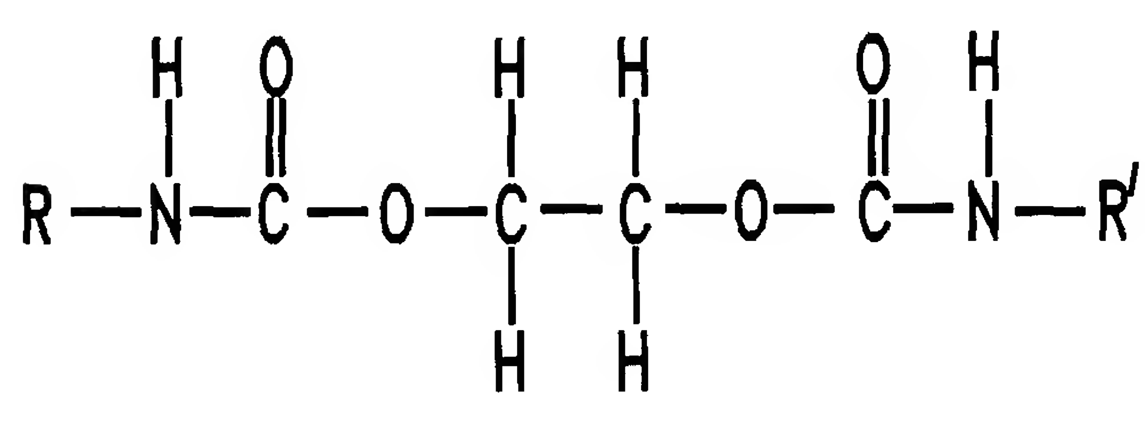
The present invention is directed primarily to urea and urethane polymers, but can be useful in the incorporation of pendant alkyl structures in other types of polymers that use an amine or alcohol groups to form the linkage. Other polymer types which can utilize this invention include, but are not limited to the following: polyamide, polyester, polycarbonate, polyether, polysiloxane, and epoxy.

DETAILED DESCRIPTION OF THE INVENTION

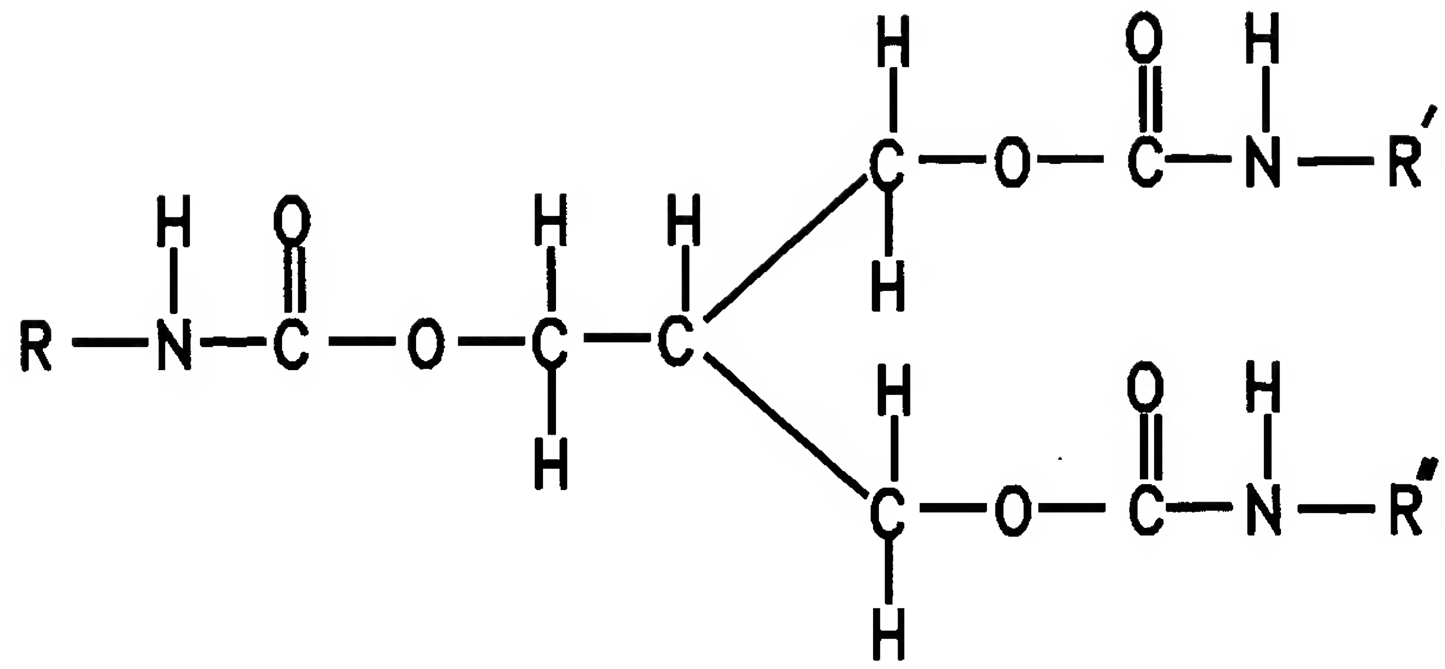
It is well known in the art to combine polyols or polyol pre-polymers with organic isocyanates and other materials to form polymers and polymeric resins. In particular, paints and coatings often contain polyurethane or other polymeric coating materials derived from an amine or alcohol functional monomer. A generic urethane has the following structure:



It is well known in the art that R and R′ can be the same or different. A typical polyurethane polymer is made up of chains of the form:



or of the form:



Multifunctional fatty compounds,such as polyamines or ethoxylated amines, can be reacted with isocyantes to form polymers or pre-polymers that have uses in coatings, films, fibers, or structural components. In particular, ethoxylated fatty acids can be combined with organic isocyanates to form polyurethane type polymers. The resulting polymer contains fatty chains that are covalently bonded pendant to the backbone of the polymer. Ethoxylated fatty acids and fatty diamines or similar compounds containing multiple isocyanate cross-linkable moieties can be mixed, with or without the aid of a co-solvent, with the polyol component of commercially available two-component systems to the extent they are soluble. In the case of polyurethane, the linked moiety is similar to that shown in Figure 1.

Figure 1. Shows synthesis of a typical polymer of the type described by this invention. R may be any alkyl or alkoxy group of between around 6 to around 22 carbons. R′ and R′′ can be the same or different, chosen from a wide range of materials,

including, but limited to, H, $-(CH2)_nH$, $-(CH2)_nNH2$, $-[(CH2)_nNH]_m(CH2)_o]NH2$, with n, m and o from 1 to 30, $-(CH2CH2O)_a-(CH2CH(CH3)O)_b-(CH2CH(CH2CH3)O)_cH$ with a, b, and c integers from 0 to 30, $-(CH2)_xH$ with x from 1-30, $-(CH2)_nN[(CH2CH2O)_a-(CH2CH(CH3)O)_b-(CH2CH(CH2CH3)O)_cH]$ $-(CH2CH2O)_a-(CH2CH(CH3)O)_b-(CH2CH(CH2CH3)O)_cH$, $-[(CH2)_nN(CH2CH2O)_a-(CH2CH(CH3)O)_b-(CH2CH(CH2CH3)O)_cH]_m(CH2)_o]N[(CH2CH2O)_a-(CH2CH(CH3)O)_b-(CH2CH(CH2CH3)O)_cH]$ $-(CH2CH2O)_a-(CH2CH(CH3)O)_b-(CH2CH(CH2CH3)O)_cH$. Together R' and R'' must contain a total of at least two terminal $-NH_2$ or -OH or a combination of either totaling at least two. The use of alkoxylated polyamines (at least three terminal -OH groups are present) as included above, produces polymers with tertiary cross linking when reacted with diisocyanates as opposed to the linear structures that result from diisocyanytes and alkoxylated primary amines. Another way to achieve teriary cross linking is to utilize a polyisocyante that has more than two isocyanate groups available for the urea/ urethane reaction.

Quaternary alkoxy amines are produced from alkoxylated amines, and contain at least two terminal -OH groups, such as the Tomah Q-series, and can be polymerized in the same manner as alkxylated amines.

Another embodiment of the invention is the use of fatty ether polyamines or ethoxylated fatty ether amines. Figure 2 Describes the case in which the fatty moiety is an alkoxy group.

A typical example of an embodiment of the invention is to combine, for example, an ethoxylated amine with a polyisocyanate. By varying the reactants, various hardnesses and flexibilities can be achieved. By varying the type of isocyanate used, the speed of cure can be adjusted. By changing the functionality of the alkyl containing component, different properties can be achieved.

It is an object of the present invention to create a class of hydrophobic urethane and urea polymers with alkyl side chains pendant to the main polymer backbone.

It is another object of the present invention to provide a way to control cross-linking in a hydrophobic polymer by controlling the amount of unsaturation present in pendant side chains.

It is another object of the present invention to provide a way to control cross-linking in a hydrophobic polymer by controlling the number amine groups or alcohol groups in the polyamine/ alkoxylated amine reactant utilized.

It is another object of the present invention to provide a way to control cross-linking in a hydrophobic polymer by controlling the number of isocyanates groups present in the polyisocyante.

It is still another object of the present invention to provide a method of making low cost sprayable hydrophobic polymeric coatings.

The preferred embodiment of the present invention is primarily directed toward polyurethane and polyurea structures, but other embodiments can include the incorporation of pendant alkyl structures in other types of polymers that use an amine, carboxcylic acid or alcohol group to form the linkage. Other polymer types which can utilize this invention include, but are not limited to, the following: polyamide, polyester, polycarbonate, polyether, polysiloxane, and epoxy.

The presence of pendant saturated or partially unsaturated fatty chains causes the resulting polymers to have hydrophobic and other desirable properties such as the ability to control the amount of final cross-linking between backbones and the pendant chains.

Examples:

EXAMPLE 1:

8g of Tomah E-17-5 (poly (5) oxyethylene isotridecyloxypropylamine) was added to 10g of Bayer Mondur E744 (pre-poly of diphenylmethane 4,4'-diisocyanate). The resulting tack free solid showed typical polymeric properties as it reacted. During the reaction, a highly fiberous and ordered plastic could be pulled from the vessel. The product liberated

heat and foamed during the reaction as well.

EXAMPLE 2:

6g of Tomah E-17-2 (poly (2) oxyethylene isotridecyloxypropylamine) was added to 10g of Bayer Mondur E744 (pre-poly of diphenylmethane 4,4'-diisocyanate). The resulting tack free solid showed typical polymeric properties as it reacted. During the reaction, a highly fiberous and ordered plastic could be pulled from the vessel. The product liberated heat, but foamed less than than Example 1. In a repeat of the reaction, the addition FB100 reduced foam substantially and resulted in a product that is much better suited to be a coating.

EXAMPLE 3:

6g of Tomah E-17-5 (poly (2) oxyethylene isotridecyloxypropylamine) was added to 10g of Bayer Mondur N3200 (pre-poly of hexamethylene diisocyanate) and 0.5g FB100 butyrate antifoam. The resulting tack free solid showed typical polymeric properties as it reacted. During the reaction, a highly fiberous and ordered plastic could be pulled from the vessel. The product reacted much slower than EXAMPLE 2 and foamed much less. This product was suitable as a coating or cast product.

EXAMPLE 4:

4.3 g Tomah Q-17-5PG (74% active isotridecyloxypropyl poly (5) oxyethylene in propylene Glycol) were added to 10g of Bayer

Mondur E 744 (pre-poly of diphenylmethane 4,4'-diisocyanate). This reaction occurred very slowly with very little visible foaming. The material did form a translucent tack free solid after eight hours.

EXAMPLE 5:

5.5g of Crison Crisamine PC-2 (poly (2) oxyethylene primary cocoamine) was added to 10g of Bayer Mondur E744 (pre-poly of diphenylmethane 4,4'-diisocyanate). The resulting tack free solid showed typical polymeric properties as it reacted. During the reaction, a highly fiberous and ordered plastic could be pulled from the vessel. The product liberated heat and foamed during the reaction but the addition of FB100 butyric antifoam helped reduce this. This material was optically clear. A slight reduction in Bayer Mindur E744 yielded a very soft flexible tack free material.

EXAMPLE 6:

7g of Crison Crisamine DC (cocodiamine)dissoloved in 40g of a 50:50 mixture of naptha and acetone was added to 10g of Bayer Mondur N3200 (pre-poly of hexamethylene diisocyanate). The products reacted very quickly, even with the solvent present and the aliphatic isocyanate. A tack free rubbery solid formed.

EXAMPLE 9:

12g of Tomah DA-17 (Isotridecyloxypropyl-1,3-diaminopropane)was

added 10g to Bayer Mondur N3200 (pre-poly of hexamethylene diisocyanate) in 40g of naptha. The reaction was almost instantaneous, white strands formed immediately upon contact and a tack free stringy mass resulted after the solvent was evaporated.

EXAMPLE 10:

10g of Crison Crisamine PC-2 (poly (2) oxyethylene primary cocoamine) was added to 5.8g of Bayer Desmodur H (hexamethylene diisocyanate, HDI). The resulting tack free solid had a straw color, but good clarity and moderate to high stiffness with essentially no foaming.

EXAMPLE 11:

10g of Crison Crisamine PC-2 (poly (2) oxyethylene primary cocoamine)was combined with 10g of Crison Crisamine DT-3 (Tris(2-hydroxyethyl)-N-tallowalkyl-1,3-diaminopropane)before being added to 12.9g of Bayer Desmodur H (hexamethylene diisocyanate, HDI). The resulting material formed a tack free solid more quickly than Example 10. The resulting solid was very elastic with good clariy and essentially no foaming.